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(54) POLYLACTIC ACID COMPOSITION HAVING ANTISTATICITY AND ITS MOLDING

(57)Abstract:

PURPOSE: To obtain the subject composition excellent in antistaticity, glossiness, transparency, etc., and useful for fibers, woven fabrics, etc., by compounding a polymer mainly containing lactic acid with a block copolymer of a polyalkylene ether with a polylactic acid in a specific weight ratio.

CONSTITUTION: This composition is a mixture composed of (A) a polymer mainly containing lactic acid [preferably, a polylactic acid of a copolymer containing a lactic acid-derived component of ≥50wt.% in the polymer] and (B) a block copolymer composed of (i) a polyalkylene ether and (ii) a polylactic acid, wherein the weight ratio of the component B is 0.3-50wt.%, preferably 0.5-30wt.%. Further, the component (i) is preferably at least the one selected from a polyethylene glycol, a polypropylene glycol and their copolymer, and the weight ratio of the component (i) is preferably 70-95wt.% in the component B. Furthermore, the component B preferably has a volume resistivity of ≤1×1010Ω.cm and a molecular weight of ≥10000.

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CLAIMS

[Claim(s)]
[Claim 1] The polylactic acid constituent of the antistatic nature characterized by being a mixed constituent containing the polymer (A) which uses a lactic acid as a principal component, and the block copolymer (B) of the polyalkylene ether and polylactic acid, and being the range whose weight ratio of said block copolymer (B) is 0.3 - 50%.
[Claim 2] The constituent according to claim 1 whose polyalkylene ether is at least one sort of things chosen from the group of "a polyethylene glycol, polypropylene glycols, and those copolymers."
[Claim 3] The constituent according to claim 1 to 2 whose weight fraction of the polyalkylene ether which constitutes the block copolymer (B) of the polyalkylene ether and polylactic acid is 70 - 95%.
[Claim 4] The constituent according to claim 1 to 3 whose volume resistivities of the block copolymer (B) of the polyalkylene ether and polylactic acid are below 1x 1010 ohm and, and cm.
[Claim 5] The constituent according to claim 1 to 4 whose mixed ratio of the block copolymer (B) of the polyalkylene ether and polylactic acid is 0.5 - 30 % of the weight.
[Claim 6] The constituent according to claim 1 to 5 whose molecular weight of the block copolymer (B) of the polyalkylene ether and polylactic acid is 10,000 or more.
[Claim 7] The constituent according to claim 1 to 6 with which the block copolymer (B) of the polyalkylene ether and polylactic acid is distributing the lactic acid which is a parent in the polymer (A) used as a principal component with the shape of a detailed particle, and a needlelike gestalt.
[Claim 8] The constituent according to claim 1 to 7 which the block copolymer (B) of the polyalkylene ether and polylactic acid is distributing fibrous [detailed], a line, and in the polymer (A) which uses as a principal component reticulated or/and the lactic acid which is a parent at the shape of a thin layer.
[Claim 9] The fiber which consists of a constituent according to claim 1 to 8, knitting, textiles, a nonwoven fabric, paper, the felt, a network, a rope, a film, a sheet, a plate, a rod, a tube, a container, various components, and other casts.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the polylactic acid of antistatic nature, and its cast.
[0002]
[Description of the Prior Art] The polymer decomposed under biodegradability or natural environment attracts attention from the standpoint of environmental protection. Especially polylactic acid is advantageous also in resource in order to use agricultural products as a raw material, and since it excels in melting moldability or thermal resistance further, it is expected most. However, since crystallinity is high and the absorptivity of crystallinity is also low, by friction or breakaway, non-denaturalized polylactic acid is charged easily and generates various static electricity troubles. For this reason, polylactic acid excellent in antistatic nature is called for.
[0003] It is common knowledge to mix a polyether especially a polyethylene glycol, or its denaturation object to synthetic resin, such as a polyamide and polyester, and to give antistatic nature (for it to be described as an antielectricity characteristic below) conventionally, to it. However, if a polyethylene glycol is mixed to polylactic acid, since both compatibility is small, it must mix quite so much for it to be mixed in the shape of [comparatively large] a particle, and acquire sufficient antielectricity characteristic, and the problem that the transparency and gloss of a cast are spoiled will produce a polyethylene glycol.
[0004]
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the improved new polylactic acid constituent with which the antielectricity characteristic which suppressed the fall of the transparency of a cast or gloss and was excellent in comparatively little mixing percentage is acquired.
[0005]
[Means for Solving the Problem and its Function] The purpose of above-mentioned this invention is attained by mixing said block copolymer (B) in the range whose weight ratio is 0.3 - 50% among the mixed constituents containing the polymer (A) which uses a lactic acid as a principal component, and the block copolymer (B) of the polyalkylene ether and polylactic acid.

[0006] It is copolymerization polylactic acid with which the polymer which uses a lactic acid as a principal component here copolymerized the polymerization ingredient of ester bonding nature in polylactic acid homopolymers, such as Pori L-lactic acid, a Pori D-lactic acid, and a Pori ratio-of-length-to-diameter-lactic acid, and them, and the component of the lactic-acid origin in a polymer says 50% of the weight or more of a thing.
[0007] Although the polyalkylene ether (polyalkylene oxide) has electrical conductivity by ether linkage, as an antielectric agent, a polyethylene glycol, polypropylene glycols, and those

copolymerization objects are excellent in the antielectricity characteristic, and especially a polyethylene glycol and its denaturation object have the most excellent antielectricity characteristic.

[0008] The description of this invention constituent is to use the block copolymer (B) of polylactic acid and the polyalkylene ether as an antielectric agent. What the polylactic acid segment (L) and the polyalkylene ether segment (E) combined with the mold of L-E by 1 to 1 is sufficient as this block copolymer, it may be combined with L-E-L and a mold like E-L-E by 2:1 or 1:2, and many segments (block) may be combined like [it is same and] L-E-L-E-L-E. moreover, between both -- the 3rd component -- as a joint -- entering -- **** -- further -- except [these] -- secondary -- degree component may be added. However, main components (50 % of the weight or more) are the polyalkylene ether and polylactic acid.

[0009] Work of the polylactic acid segment in an antielectric agent (B) raises compatibility with the polylactic acid (A) which is an antielectric agent (B) and a parent (matrix) polymer. An antielectric agent is minutely distributed in a parent polymer, and the cast excellent in an antielectricity characteristic, transparency, gloss, etc. is obtained, so that both compatibility is high. However, when there are too many polylactic acid segments in an antielectric agent, a polyether segment decreases and an antielectricity characteristic comes to be inferior. For this reason, 50 - 97% of the weight fraction of the polyalkylene ether component in an antielectric agent (B) is desirable, and is desirable. [especially 70 - 95% of] That is, 5 - 30% of especially the weight fraction of the polylactic acid component in an antielectric agent (B) is desirable 3 to 50%.

[0010] although especially the molecular weight of an antielectric agent (B) is not limited -- a ** grade -- a large thing is desirable, for example, 3,000 especially or more are desirable 1,000 or more molecular weight, it is still more desirable, 10,000-200,000 are the largest, and 5,000 or more are used.

[0011] Manufacture of the antielectric agent (B) used for this invention is comparatively easy. For example, the end of the method of one is blocked, if the polymerization of the lactide is carried out for the polyethylene glycol which has a hydroxyl group in a piece end as a polymerization initiator of a lactide, the block copolymer of a L-E mold will be obtained, and if the polyethylene glycol which has a hydroxyl group in both ends is made into a polymerization initiator, the block copolymer of L-E and an L type will be obtained. 2 functionality compounds, such as a dicarboxylic acid anhydride, a dicarboxylic acid chloride, and diisocyanate, can be made to be able to react to the polyethylene glycol and polylactic acid which similarly have a hydroxyl group in a piece end or both ends, and both can be connected with them. Furthermore, the addition polymerization of alkylene oxide, for example, the ethylene oxide, is carried out to the polylactic acid which has a hydroxyl group at the end, and a polyethylene-glycol chain can be formed and it can consider as a block copolymer. In these reactions, it is also comparatively easy to control the molecular weight of a polyalkylene ether block and the molecular weight of a polylactic acid block. For example, the polyethylene-glycol 80 section of molecular weight 8,000 and the lactide 20 section being perfect and the block copolymer of L-E and an L type which the polylactic acid (oligomer) of a degree of polymerization 10 combined with the both ends of the polyethylene glycol of molecular weight 8,000 when reacting to homogeneity (polymerization) should be obtained. Although variation arises considerably in fact although it becomes so as an average value, and the mixture of various kinds of compounds is obtained, the principal component of the mixture is the block copolymerization object of a polyethylene glycol and polylactic acid, and does not interfere at all, using mixture as an antielectric agent as it is.

[0012] Although you may remain as it is, when functional groups, such as hydroxyl groups, such as a molecule end of an antielectric agent, and a carboxyl group, are made to react with a monofunctional machine nature compound, are ****(ed) and are stabilized, they are still more

desirable.
[0013] The electrical conductivity of an antielectric agent (B) is so good that it is high. Generally the volume resistivity of a polyethylene glycol is 1x109. It is an ohm and cm extent (it measures by 25 degrees C, 40%RH, and 1kV or less of direct currents), and if it copolymerizes with polylactic acid, it will increase to 1x1010 ohm and cm extent. However, the compound which is easy to ionize in these, for example, alkyl benzene sodium sulfonate etc., is mixed about 2 to 20%, and it is a volume resistivity 1x10 8-9 What was made into below an ohm and cm extent is suitable. The constituent of this invention and especially the volume resistivity of a cast have desirable 1x1011 ohm and cm below 1x1012 ohm and cm. Antioxidants, such as a HINDATO phenol, various stabilizers, an ultraviolet ray absorbent, and other additives can be added to an antielectric agent (B) as a secondary additive.
[0014] Mixing to the parent polymer (A) of an antielectric agent (B) is arbitration, such as application of mechanical agitation and a quiescence mixer, and both concomitant use. It is common to perform mixing after the polymerization of a parent polymer (A). When it adds in a polymerization raw material or a polymerization process, it copolymerizes in response to mutual, and an antielectricity characteristic may be lost or it may fall. The outstanding antielectricity characteristic needs to exist independently with gestalten, such as the shape of the very fine particle which the antielectric agent distributed in the parent polymer, a microfilament, network structure, and a thin layer. It causes [it is necessary to use quite a lot of polyalkylene ether, and] degradation of physical properties and is not desirable if a polyalkylene ether block is built into a parent polymer molecule by copolymerization.
[0015] Mixing by mechanical agitation can be performed using various agitators, a screw extruder, a biaxial kneading machine, a kneader, a gear pump, etc. On the other hand, if it mixes statically by division of flow, and repetition of junction (compound) using a quiescence mixer, an antielectric agent (B) can be minutely distributed in a parent polymer (A) with the structure which continues [shape / of the shape of a thin layer, and a microfilament]. as the example of a quiescence mixer -- this invention person JP,47-15526,B -- said -- 47-15527 -- said -- 47-15528 -- said -- the thing indicated by 47-15533 etc., the thing indicated by JP,47-34166,A are raised. Mechanical agitation and a quiescence mixer can also be used together. For example, if measuring liquid sending is carried out with a gear pump after multilayer mixing with a quiescence mixer, it will be mechanically agitated in a pump part and an antielectric agent will be distributed in the shape of [detailed] a particle. of course, the direction of continuation structure boils an antielectricity characteristic markedly, and is excellent, it is the mixing percentage of the antielectric agent of 1 / 5 - 1/10 of granular (discontinuity) structure, and an equivalent antielectricity characteristic is acquired in many cases.
[0016] Although the mixing percentage of an antielectric agent (B) in this invention constituent changes with presentations and volume resistivities of the conductivity of an antielectric agent, and an antielectric agent, in many cases, 0.5 - 30% of range is especially suitable for it 0.3 to 50% of the weight. As mentioned above, if the antielectric agent is distributed and mixed with continuation structures, such as the shape of fibrous, reticulated, and a thin film, it will excel in electrical conductivity and comparatively little mixing percentage, for example, the antielectricity characteristic which was especially excellent in 0.5 - 5%, will be obtained 0.3 to 10%. On the other hand, if the antielectric agent is distributed and mixed with the shape of a particle, the shape of a long and slender particle, and which needlelike discontinuous structure, comparatively many antielectric agents are needed, for example, 5 - 30% of mixing percentage is especially suitable 3 to 50%. Both middle mixing percentage is suitable in it being discontinuous at mixed construction with continuation, for example, the structure where fibrous is intermingled as it is granular.
[0017] In this invention constituent, other components other than the polymer (A) which uses a lactic acid as a principal component, and an antielectric agent (B) may be added secondarily.

As an example of a secondary additive, a stabilizer, an antioxidant, an ultraviolet ray absorbent, a pigment, a coloring agent, various inorganic particles, various fillers, water repellent, a hydrophilic agent, a release agent, a plasticizer, a physiological active substance, antiseptics, an antimicrobial agent, and a foaming agent and other likes are raised.
[0018] In the following examples and this inventions, unless it mentions specially, a weight ratio and a weight fraction show the section and %. The molecular weight of the polymer which uses a lactic acid as a principal component is chloroform of a sample. It is GPC analysis of 0.1% solution, and is molecular weight. It is the weighted mean value of the distribution of a high polymer or less except 500.
[0019]
[Example]
With example 1 molecular weight 8,000, Ciba-Geigy IRUGA NOx 1010 is mixed as a polymerization catalyst, they mix 0.1% as 0.1% of tin octylate, and an anti-oxidant to the polyethylene-glycol 80 section of a hydroxyl group, and the L-lactide 20 section of 99% or more of optical purity, and both ends consider the block copolymerization object (volume-resistivity 3x109 an ohm and cm) of a polyethylene glycol and polylactic acid which was made to react for 45 minutes and was obtained at 180 degrees C among nitrogen-gas-atmosphere mind as the antielectric agent AS 1.
[0020] As opposed to L-lactide of 99% or more of optical purity 0.03% of tin octylate, Mix a titanium oxide particle (crystalline-nucleus agent) with a diameter of 0.05 micrometers, and the biaxial continuation mixing liquid-sending machine with which two screws gear mutually is used. The screw group which is made to react for an average of 30 minutes continuously at 180 degrees C among nitrogen-gas-atmosphere mind, then adds tin octylate 0.1%, and gears mutually, The biaxial kneading machine which consists of the churning elements of an ellipse (2 flight molds) which gear mutually is used. The antielectric agent AS 1 which carried out the polymerization for 17 minutes at 190 degrees C, was fused and was made into the moisture content of 5 ppm or less from the last Bento It added and mixed 7% to the polymerization system, and further, after passing the ****** ellipse cylinder and mixing 60 KENIKKUSU static mixers, it extruded from the mouthpiece, water cooled, solidified and cut, and the chip C1 was obtained.
[0021] The chip C1 was heat-treated in 120-degree-C nitrogen for 12 hours, heat treatment (solid state polymerization) was carried out at 140 more degrees C for 48 hours, and the chip C2 was obtained. 152,000 and the amount of residual monomers (lactide) of the mean molecular weight of a chip C2 were 0.3%.
[0022] The chip C2 was fused with the 200-degree C screw extruder, and it spun from 0.2mm of apertures, and an orifice with a temperature of 195 degrees C, and after [cooling] oiling was carried out in air, and it rolled round at the rate of 800 m/min, then, extended 3.7 times at the extension temperature of 80 degrees C, it heat-treated at 120 degrees C under stress, and the extension yarn Y1 of the fineness of 75 deniers / 24 filament was obtained.
[0023] The extension yarn obtained like extension yarn Y1 without an antielectric agent's adding AS1 is set to Y2.
[0024] The tube knitting K1 was obtained for extension yarn Y1 using the small round-braid machine with a cylinder diameter of 80mm. It is JIS about knitting K1. L After washing 3 times using household detergent and a home electric washing machine according to 1094-1988, rinsing enough in a stream and leaving it all over the thermostatic chamber of 25 degrees C and 33%RH after 2-hour desiccation with 80-degree C hot air drying equipment for 24 hours, the frictional electrification nature was measured.
[0025] measurement of frictional electrification -- this invention person etc. -- developing -- JIS L it specifies to 1094-1988 as a referring method "a frictional electrification discharge curve measuring method" -- having -- **** -- fiber Japan Society of Mechanical Engineers vol. -- it

was based on the approach indicated to 40, No.4, p181-188 (1987), and JP,62-11303,B. That is, the washed sample is cut in die length of 12cm, and width of face of 12cm, and it attaches in a metal plate with a hole with a diameter of 7cm, and after using as a friction cloth wash, desiccation, and the wool textiles that carried out gas conditioning and rubbing them 10 times manually on a wooden base, it pulls away from a base, and moves in front of a potential detector, and account record of ** of a friction band electrical potential difference and its decay curve is carried out with a recorder. [as well as a test piece]

[0026] The frictional electrification nature of the knitting K2 obtained using extension yarn Y2 was measured like knitting K1. Furthermore, for the comparison, it mixed 7% by having made the polyethylene glycol of molecular weight 20,000 into the antielectric agent, and the electrification nature of knitting K3 obtained like knitting K1 below was measured.

[0027] The band electrical potential difference immediately after friction of knittings K1, K2, and K3 and the band electrical potential difference 1 minute after friction are shown in Table 1. The knitting K1 by this invention had the low insulating value of a band electrical potential difference (especially after 1 minute) compared with the examples K2 and K3 of a comparison, and was excellent in the antielectricity characteristic so that it might see to Table 1.

[0028]

[Table 1]

編物	帯電圧（kV）		備考
	摩擦直後	摩擦1分後	
K1	−8．1	−1．3	本発明
K2	−14．4	−14．1	比較例
K3	−12．0	−3．2	比較例

Let the polylactic acid and the block copolymerization object of a polybutylene horse mackerel peat with which example 2 molecular-weight both ends carried out melting copolymerization for 45 minutes, and obtained the polybutylene horse mackerel peat 15 section of a hydroxyl group, and the L-lactide 85 section of 99% or more of optical purity at 180 degrees C about 20,000 be a polymer P3. The molecular weight of a polymer P3 is 163,000, and carried out melt spinning of this with the screw extruder with a temperature of 200 degrees C. At the time of spinning, within the spinneret which carried out the internal organs of the quiescence mixer, it mixed 0.7% and spinning of the antielectric agent AS 2 which carried out melting dehydration independently was carried out. the antielectric agent AS 2 -- AS1 of an example 1 -- sodium dodecylbenzenesulfonate -- 15% -- mixing -- a volume resistivity -- 1x108 up to -- you make it fall A quiescence mixer is what this invention person etc. indicated to JP,57-20842,B, and connects a mixed component to a 12-piece serial. The antielectric agent mixed in the shape of a multilayer (the shape of a thin layer) with the quiescence mixer is divided by the final filter in front of an orifice, and it distributes in the shape of a multipoint, and it serves as a gestalt of the shape of a microfilament which continues in the die-length direction substantially (line) on the fiber cross section. (Even if it uses what made the mixed component of the static mixer of U.S. KENIKKUSU the 10-12-piece serial, the almost same thing is obtained) . The frictional electrification nature of extension, heat treatment, ****, wash, desiccation, and the knitting K4 that carried out gas conditioning was measured for the fiber which carried out spinning like the extension yarn Y1 of an example 1, and knitting K1, and the result of Table 2 was obtained. A high antielectricity characteristic is acquired by mixing of the antielectric agent of **** small quantity by mixing the compound of ionization nature in an antielectric agent, and mixing an antielectric agent in the shape of a continuation microfilament in a parent polymer so that it

may see to Table 2. In addition, about the gloss and the feeling of transparence of knitting, the knittings K1 and K4 by this invention were excellent, and the knittings K2 and K3 of the example of a comparison were inferior in gloss and a feeling of transparence. (This difference becomes still larger in a film or a thick cast) .

[0029]

[Table 2]

	帯電圧（kV）		
編物	摩擦直後	摩擦1分後	備考
K4	−4．0	−0．4	本発明

[0030]

[Effect of the Invention] By this invention, various mold goods excellent in an antielectricity characteristic, gloss, and transparency are obtained easily. For example, fiber, knitting, textiles, a nonwoven fabric, paper, a rope, a network, a rope, a film, a sheet, a plate, a rod, various containers, a tube, various components, and various kinds of other casts are raised. Contamination by adhesion of the failure by electrification of various casts, i.e., dust, and bacteria, a skirt board, trousers, underwear, etc. coil, malfunction of the electronic equipment by ignition of the combustible by spark discharge, explosion, and spark discharge, failure, etc. are reduced or prevented by the antielectricity characteristic constituent by this invention, and outstanding fiber with still higher gloss and transparency, a film, and a cast are obtained with it. Moreover, since an elastic modulus is small and this invention antielectric agent (B) is excellent in impact absorptivity, as for this invention constituent and a cast, flexibility and shock resistance are improved as a secondary effect.

[Translation done.]